# Acid Responsive Hydrogen-Bonded Organic Frameworks

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8. References

#### 1. General

All reagents and solvents were used as received from commercial suppliers. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured by JEOL 400 YH (400 MHz) spectrometer. Residual proton and carbon of deuterated solvents were used as internal standards for the measurements (for <sup>1</sup>H NMR, CDCl<sub>3</sub>,  $\delta = 7.26$  ppm; DMDO-*d*<sub>6</sub>,  $\delta = 2.50$  ppm: for <sup>13</sup>C NMR, CDCl<sub>3</sub>,  $\delta = 77.00$  ppm; DMSO-*d*<sub>6</sub>,  $\delta = 39.50$  ppm). Mass spectrum data were obtained from a JEOL JMS-700 instrument or autoflex III Bruker. Thermo gravimetric (TG) analysis were performed on Rigaku TG8120 under an N<sub>2</sub> purge (100 mL/min) at a heating rate of 5 Kmin<sup>-1</sup>. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima-IV (40 kV, 44 mA) using graphite-monochromatized Cu-Ka radiation ( $\lambda = 1.54187$  Å) at room temperature. A scan rate is 2.0 °/min.

Single crystal X-ray measurement and analysis. Diffraction data of CPHATN-1(TCB), CPHATN-1a, CPHATN-NP(DMAc), and CPHATN-NP(NMP) were collected on a two-dimensional X-ray detector (PILATUS 200K/R) equipped in Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54187$  Å). The cell refinements were performed with a software CrysAlisPro 1.171.38.410.<sup>S1</sup> SHELXT<sup>S2</sup> was used for the structure solution of the crystals. All calculations were performed with the observed reflections [I > 2 $\sigma$ (I)] with the program CrystalStructure crystallographic software packages, except for refinement which was performed by SHELXL.<sup>S3</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. SQUEEZE function equipped in the PLATON program<sup>S4</sup> was used to remove severely disordered solvent molecules in voids.

Variable temperature (VT) PXRD measurement. Crystalline bulk of CPHATN-1(TCB) placed on an aluminum substrate was subjected to VT-PXRD measurement under the air atmosphere. PXRD data were collected on a Rigaku Ultima-IV using graphite-monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.54187$  Å) with a temperature control unit. Temperature of the sample was increased from room temperature to 633 K with a rate of 1 K/min. During temperature increasing, XRD patterns ranged from 2° to 17° was repeatedly recorded with a scan rate of 3 °/min. Therefore, each PXRD scan has a temperature width of 5 K.

**Sorption/desorption experiment:** Activation of **CPHATN-1(TCB)** was performed under vacuum condition (0.2 kPa) for 48 h at 463 K to give **CBPHAT-1a** for sorption experiments. Gas sorption measurements were performed on BELSORP-max (BEL, Japan). The adsorption isotherms of N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub> were corrected at 77K, 77 K, 195 K and 77 K, respectively.

**Solid state spectroscopy.** The steady-state UV-visible absorption and emission spectra have been recorded using JASCO V-670 and FluoroMax-4 (Jobin-Yvon) spectrophotometers, respectively. Picosecond emission decays were measured using a time-correlated single photon counting (TCSPC) system.<sup>S5</sup> For the excitation at 371 nm, the samples were excited using a 40-ps pulsed diode laser centred at 371 nm (<5 mW, 40 MHz repetition rate) and the instrument response function (IRF) was ~ 70 ps. The IRF of the system was measured using a standard LUDOX

(Sigma-Aldrich) suspension in a 1 cm cell. The decays were deconvoluted and fitted to a multiexponential function using the FLUOFIT package (PicoQuant) allowing single and global fits. The quality of the fit was estimated by  $\chi^2$ , which was always below 1.2, and the residual distribution.

The fluorescence lifetime imaging (FLIM) measurements were performed on a MicroTime 200 confocal microscope (PicoQuant). As an excitation source, we used a diode laser with an excitation wavelength of 390 nm (40 ps full width at half-maximum of intensity). Briefly, it consists of inverse Olympus IX 71 microscope equipped with a water immersion objective (x60 NA1.2, Olympus) and 2D piezo scanner (Physik Instrumente). The emitted light is then focused on a pinhole of 50 µm and later collimated to two independent single photon avalanche photodiodes (Micro-Photon-Devices) for time-resolved measurements. The emission spectra were collected through Shamrock SR-303i (Andor Technology) imaging spectrograph and detected by Andor Newton EMCCD camera (Andor Technology). For the anisotropy measurements the light was passed through a polarizing beam-splitter that allows for the simultaneous detection of the parallel and perpendicular parts of the emission. A G-factor of 1.2, accounting for differences in the detection sensitivity for both polarizations in the setup, was used in the calculation of the anisotropy. Moreover, to calculate the histogram of anisotropy, we used SymPhoTime Analysis program (which is facilitated by PicoQuant), which calculates the static anisotropy on an image. The analysis is based on the work of Schaffer group. The limits for the anisotropy are -0.5 to 1.0, in which -0.5 correspond to perpendicular orientation and 1.0 to parallel. The emission signal was collected using one long pass filters (HQ430LP Chroma).

Femtosecond time-resolved emission decays were collected using a fluorescence up-conversion technique with a reflection mode disposition of the system. The setup of the equipment and a detailed description of the system have been previously published.<sup>S6</sup> Briefly, the sample was excited at 400 nm and gated the emission at different observation wavelengths using the 800 delayed probe. To analyse the fs-transients, we deconvoluted a multiexponential function with the IRF (~250 fs) to fit the experimental data.

**Detailed procedure for soaking experiments of CPHATN-1a in 37% HCl.** Crystalline bulk of **CPHATN-1a** was soaked in 37%-HCl at room temperature for 24 h. The crystalline bulk was collected by membrane filter, and the wet brown bulk was placed on glass substrate and subjected to PXRD measurement (Figure 4 top, thin line). Removal of aqueous solution of HCl was accomplished by heating on hot plate at 423 K for 1 h under ambient pressure. The brown bulk kept its morphology but just turned into yellow bulk. The treated bulk on the substrate was again subjected to PXRD measurement (Figure 4 top, bold line).

#### 2. Synthesis and crystallization of CPHATN



1,2-dibromo-4,5-diaminobenzene Diaminobenzene derivative 2. (10.0)37.6 mmol), g, 4-methoxycarbonylphenylbronic acid (16.9 g, 94.1 mmol), Pd(dppf)<sub>2</sub>Cl<sub>2</sub> (2.68 g, 3.66 mmol), and K<sub>2</sub>CO<sub>3</sub> (15.6 g, 113 mmol) was added into a degassed solvent of toluene (600 mL), water (300 mL), and 1,4-dioxane (300 mL) and stirred for 26 h at 85 °C. The product was extracted by CHCl<sub>3</sub>, washed with water and brine, dried over MgSO<sub>4</sub>, and concentrated in vacuo. Purification was conducted by column chromatography (silica gel, CHCl<sub>3</sub>: AcOEt : Et<sub>3</sub>N = 17 : 3 : 1 v/v/v) to give 4 (10.2 g, 72%) as a brown solid. 4: Mp. 191 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.84 (d, J = 7.2 Hz, 4H), 7.13 (d, J = 8.0 Hz, 4H), 6.49 (s, 2H), 3.88 (s, 6H), 3.55 (br, 4H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 40 °C) δ154.7, 146.2, 134.7, 131.6, 129.8, 129.2, 127.7, 118.6, 52.00 ppm. HR-MS (FAB+) *m/z* calc. for [M+1]<sup>+</sup> C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: 376.1423; found: 376.1418.

Methyl ester 4. 2 (10.1 g, 8.49 mmol) and 3 (2.10 g, 12.5 mmol) are stirred in acetic acid (400 mL) for 36 h at 100 °C. After cooled to room temperature, the precipitate was separated through filtration and washed with ethanol. The product was dissolved in CHCl<sub>3</sub>, passed through a filter paper, and concentrated in vacuo to yield pure 6 (7.54 g, 94%) as a greenish yellow soild. 4: Mp. >300 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 40 °C)  $\delta$  8.78 (s, 6H), 8.02 (d, *J* = 8.0 Hz, 12H), 7.41 (d, *J* = 8.0 Hz, 12H), 3.95 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 40 °C)  $\delta$  166.6, 144.7, 144.2, 143.9, 143.0, 131.9, 129.9, 129.8, 129.7, 52.2 ppm. HR-MS (MALDI) *m/z* calc. for [M]<sup>-</sup> C<sub>72</sub>H<sub>48</sub>N<sub>6</sub>O<sub>12</sub>: 1188.3330; found: 1188.3372.

**CPHATN.** To a solution of methyl ester derivative **4** (57.5 mg, 0.0484 mmol) dissolved in THF (14 mL) was added 10% KOH<sub>aq.</sub> (1.5 mL). The reaction mixture was stirred at 60 °C for 32 h. During this, water (6 mL) was added in several portions. THF was removed in vacuo and the resulting water layer was filtered through filter paper. 6M HCl was added dropwise into the filtrate to be acidified. The resulting yellow precipitate was filtered, washed with water and ethanol, and dried in vacuo to give **CPHATN** (44.5 mg, 85%) as a brown solid. **CPHATN:** Mp. >300 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 100 °C)  $\delta$  8.40 (s, 6H), 7.90 (d, *J* = 8.2 Hz, 12H), 7.45 (d, *J* = 8.2 Hz, 12H) ppm. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 100 °C)  $\delta$  166.2, 143.8, 143.1, 142.7, 141.1, 130.3, 129.9, 129.5, 129.1, 128.8, 128.6 ppm. HR-MS (MALDI) *m/z* calc. for [M]<sup>-</sup> C<sub>66</sub>H<sub>36</sub>N<sub>6</sub>O<sub>12</sub>: 1104.2391; found: 1104.2386.



**Figure S1.** Crystal structures of nonporous crystals of **CPHATN**. (a) **CPHATN-NP(DMAc)**. (b) **CPHATN-NP(NMP)**. Color: light cyan; **CPHATN**, red; solvent molecules *N*,*N*-dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), and 1,2,4-trichlorobenzene (TCB).

| -                                 |   | · · · ·                              |
|-----------------------------------|---|--------------------------------------|
|                                   | CPHATN-NP(DMAc)                             | CPHATN-NP(NMP)                       |
| Formula                           | $(C_{66}H_{36}N_6O_{12}) \cdot 5(C_4H_9NO)$ | $3(C_{66}H_{36}N_6O_{12})$           |
|                                   |   | $\cdot C_6H_3Cl_3\cdot 12(C_4H_9NO)$ |
| Fw                                | 3823.61                                     | 4686.05                              |
| crystal system                    | triclinic                                   | triclinic                            |
| space group                       | <i>P</i> -1                                 | <i>P</i> -1                          |
| Z/ Z'                             | 2/1   | 2/1                                  |
| a                                 | 7.55733(14)                                 | 23.53390(13)                         |
| b                                 | 20.5126(7)                                  | 25.94850(12)                         |
| С                                 | 26.9565(9)                                  | 27.49620(15)                         |
| α                                 | 71.418(3)                                   | 108.6710(4)                          |
| β                                 | 83.519(2)                                   | 100.8300(5)                          |
| γ                                 | 82.560(2)                                   | 108.2700(5)                          |
| V                                 | 3916.2(2)                                   | 14309.08(16)                         |
| T / K                             | 213   | 223                                  |
| Number of reflection (obs/uniq)   | 35462/15186                                 | 187607/52815                         |
| <i>R</i> 1 ( $I > 2.0\sigma(I)$ ) | 0.0465                                      | 0.0788                               |
| wR(all)                           | 0.1323                                      | 0.2597                               |
| CCDC Nos.                         | 1877480                                     | 1886521                              |
|                                   |   |                                      |

 Table S1. Crystal data of CPHATN-NP(DMAc) and CPHATN-NP(NMP)

### 3. Activation of CPHATN-1(TCB)



**Figure S2.** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) spectrum of **CPHATN-1a** activated under vacuum condition at 190 °C for 72 h.



Figure S3. PXRD pattern of CPHATN-1a activated under vacuum condition at 190 °C for 72 h.



Figure S4. PXRD pattern of a desolvated sample of CPHATN-NP(NMP), as well as simulated pattern of CPHATN-NP(NMP) based on single crystalline data and experimental pattern of CPHATN-1a. Desolvation of the solvate crystal was performed under vacuum condition at 190 °C for 72 h. These results indicate that a framework similar with CPHATN-1a can form by desolvation of the nonporous solvate crystal [CPHATN-NP(NMP)], although the crystallinity is lower than CPHATN-1a, judging from the broaden PXRD pattern.



**Figure S5.** Comparison between **CPHATN-1a** and **CPHATN-1(TCB)**. Conformationally frustrated carboxy dimers (green parts) have different conformations each other.

| Table S2. Crysta                  | l data of <b>CPHATN-1(TCB)</b> at | nd CPHATN-1a              |
|-----------------------------------|-----------------------------------|---------------------------|
|                                   | CPHATN-1(TCB)                     | CPHATN-1a                 |
| Formula                           | $(C_{66}H_{36}N_6O_{12})$         | $(C_{66}H_{36}N_6O_{12})$ |
| Fw                                | 1105.04                           | 1105.04                   |
| crystal system                    | triclinic                         | triclinic                 |
| space group                       | <i>P</i> -1                       | <i>P</i> -1               |
| Z/ Z'                             | 2/1                               | 2/1                       |
| a                                 | 7.27754(17)                       | 7.3893(4)                 |
| b                                 | 20.8039(4)                        | 19.3980(11)               |
| С                                 | 21.7135(4)                        | 21.3787(10)               |
| α                                 | 76.5118(17)                       | 80.108(4)                 |
| β                                 | 89.6714(17)                       | 88.822(4)                 |
| γ                                 | 86.3993(18)                       | 82.022(5)                 |
| V                                 | 3190.33(12)                       | 2989.6(3)                 |
| T/K                               | 213                               | 93                        |
| Number of reflection (obs/uniq)   | 27298/ 12287                      | 26515/11556               |
| <i>R</i> 1 ( $I > 2.0\sigma(I)$ ) | 0.0808                            | 0.1163                    |
| wR(all)                           | 0.2490                            | 0.3618                    |
| CCDC Nos.                         | 1877481                           | 1877479                   |

#### 4. Gas sorption experiment



**Figure S6**. N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, and O<sub>2</sub> sorption isotherms of **CPHATN-1a** at low temperature. N<sub>2</sub> (black circle) at 77 K, CO<sub>2</sub> (green triangle) at 195 K, O<sub>2</sub> (blue square) at 77 K, and H<sub>2</sub> (red diamond). Solid symbol: absorption. Open symbol: desorption.



Figure S7. BET plot for N<sub>2</sub> absorption isotherm at 77 K.



**Figure S8.** Pore size distribution calculated by the NLDFT method. The calculation was performed based on N<sub>2</sub> absorption isotherm at 77 K.

#### 5. Photophysical analysis of CPHAT-1a.



Figure S9. UV-visible absorption and excitation spectra of CPHATN-1a in solid state. The observation wavelengths are shown in the inset.



**Figure S10.** Time-resolved emission-spectra (TRES) of the ensemble solid of **CPHATN-1a**. The excitation wavelength was 371 nm and gating at the indicated delay times.



**Figure S11.** Magic-angle emission decays of the ensemble solid of **CPHATN-1a**, upon excitation at a) 433 and b) 470 nm, and recording at the indicated wavelengths. The solid lines are from the best global fit using a multiexponential function. The insets show a zoom of the decays at short times.



**Figure S12.** Representative femtosecond emission transients of **CPHATN-1a** in solid state upon excitation at 400 nm. The observation wavelengths are indicated in the inset. The solid lines are from the best fit using a multiexponential function.



**Figure S13.** a) Fluorescence image of **CPHATN-1a** crystals. b) Emission spectra of different points of the crystals. c) Emission decays at selected spectral range using two different filters. For detector 1, we used a FF01-625-32-25 Chroma filter, and for detector 2 we used a FF01-503-40-25 Chroma filter. The solid lines are from the best-fit using a multiexponential function. d) Histogram of the emission anisotropy for the related image. The excitation wavelength was 390 nm.



**Figure S14.** a) Fluorescence image of **CPHATN-1a** crystals. b) Emission spectra of different points of the crystals. c) Emission decays at selected spectral range using two different filters. For detector 1, we used a FF01-625-32-25 Chroma filter, and for detector 2 we used a FF01-503-40-25 Chroma filter. The solid lines are from the best-fit using a multiexponential function. d) Histogram of the emission anisotropy for the related image. The excitation wavelength was 390 nm.

| Sample                         | λ <sub>obs</sub><br>(nm) | τ1 (ps)<br>±30 ps | A <sub>1</sub> | <b>C</b> 1 | τ2 (ps)<br>±50 ps | A2 | <b>C</b> 2 | τ3 (ns)<br>±0.2 ns | <b>A</b> 3 | C3 |
|--------------------------------|--------------------------|-------------------|----------------|------------|-------------------|----|------------|--------------------|------------|----|
|                                | 490                      |                   | 80             | 57         |                   | 20 | 43         | 2.40               | -          | -  |
|                                | 500                      |                   | 80             | 57         | 540               | 20 | 43         |                    | -          | -  |
|                                | 510                      |                   | 84             | 60         |                   | 16 | 40         |                    | -          | -  |
|                                | 530                      |                   | 85             | 59         |                   | 15 | 37         |                    | -          | -  |
| SOLID OL                       | 550                      | 170               | 79             | 48         |                   | 19 | 40         |                    | 2          | 12 |
| $\lambda_{exc}$ =433 nm        | 570                      |                   | 71             | 34         |                   | 25 | 40         |                    | 4          | 26 |
|                                | 590                      |                   | 62             | 22         |                   | 30 | 37         |                    | 8          | 41 |
|                                | 610                      |                   | 45             | 14         |                   | 42 | 34         |                    | 13         | 52 |
|                                | 650                      |                   | 22             | 6          |                   | 50 | 26         |                    | 28         | 68 |
|                                | 500                      |                   | 78             | 51         |                   | 22 | 49         |                    | -          | -  |
|                                | 510                      |                   | 73             | 43         |                   | 27 | 57         | 2.40               | -          | -  |
| Ensemble                       | 530                      |                   | 83             | 57         |                   | 15 | 37         |                    | 1          | 6  |
| solid of                       | 550                      | 170               | 79             | 48         | 5(0)              | 19 | 39         |                    | 2          | 13 |
| CPHATN-1a                      | 570                      | 170               | 71             | 33         | 300               | 25 | 39         | 2.49               | 4          | 28 |
| $\lambda_{exc}=470 \text{ nm}$ | 590                      |                   | 63             | 22         |                   | 29 | 36         |                    | 8          | 42 |
|                                | 610                      |                   | 53             | 14         |                   | 33 | 31         |                    | 14         | 55 |
|                                | 650                      |                   | 40             | 7          |                   | 37 | 25         |                    | 23         | 68 |

**Table S3.** Values of time constants ( $\tau$ i), normalized (to 100) pre-exponential factors (ai) and contributions (ci= $\tau$ i x ai) obtained from a global multiexponential fit of the emission decays of the ensemble solid of **CPHATN-1a**, upon excitation at 433 and 470 nm and observation as indicated.

| Point | Detector | τ1 (ps)<br>±50 ps | A <sub>1</sub> | τ <sub>2</sub> (ns)<br>±0.2 ns | A <sub>2</sub> |
|-------|----------|-------------------|----------------|--------------------------------|----------------|
| 1     | 1        | 250               | 97             | 0.5                            | 3              |
| 1     | 2        | 600               | 84             | 2.7                            | 16             |
| 2     | 1        | 250               | 98             | 0.6                            | 2              |
| Z     | 2        | 550               | 87             | 3.0                            | 13             |
| 2     | 1        | 300               | 98             | 0.5                            | 2              |
| 3     | 2        | 540               | 90             | 2.8                            | 10             |
| 4     | 1        | 280               | 98             | 0.5                            | 2              |
|       | 2        | 580               | 89             | 2.8                            | 11             |
| 5     | 1        | 220               | 97             | 0.6                            | 3              |
|       | 2        | 560               | 90             | 3.0                            | 10             |
| 6     | 1        | 230               | 98             | 0.5                            | 2              |
| 0     | 2        | 550               | 90             | 2.9                            | 10             |
| 7     | 1        | 240               | 96             | 0.5                            | 4              |
| /     | 2        | 540               | 88             | 2.7                            | 12             |
| 8     | 1        | 290               | 98             | 0.5                            | 2              |
|       | 2        | 550               | 89             | 3.0                            | 11             |
| 0     | 1        | 300               | 96             | 0.6                            | 4              |
| 9     | 2        | 600               | 85             | 3.0                            | 15             |

Table S4. (Continued)

(a)

| Point | Detector | τ1 (ps)<br>±50 ps | A <sub>1</sub> | τ <sub>2</sub> (ns)<br>±0.2 ns | A <sub>2</sub> |
|-------|----------|-------------------|----------------|--------------------------------|----------------|
| 1     | 1        | 280               | 98             | 0.6                            | 2              |
| 1     | 2        | 550               | 86             | 3.0                            | 14             |
| 5     | 1        | 270               | 98             | 0.5                            | 2              |
| 3     | 2        | 500               | 88             | 2.8                            | 12             |
| 6     | 1        | 290               | 96             | 0.5                            | 4              |
| 0     | 2        | 600               | 84             | 3.0                            | 16             |
| 8     | 1        | 290               | 97             | 0.5                            | 3              |
|       | 2        | 570               | 87             | 2.9                            | 13             |
| 13    | 1        | 280               | 98             | 0.5                            | 2              |
|       | 2        | 600               | 86             | 3.0                            | 14             |
| 1.4   | 1        | 240               | 98             | 0.5                            | 2              |
| 14    | 2        | 510               | 87             | 2.7                            | 13             |
| 15    | 1        | 300               | 98             | 0.5                            | 2              |
| 15    | 2        | 550               | 86             | 2.7                            | 14             |
| 17    | 1        | 250               | 98             | 0.5                            | 2              |
| 17    | 2        | 540               | 91             | 2.7                            | 9              |
| 20    | 1        | 250               | 97             | 0.5                            | 3              |
| 20    | 2        | 600               | 84             | 2.8                            | 16             |

Table S4. (Continued)

| Point | Detector | τ1 (ps)<br>±50 ps | A1 | τ <sub>2</sub> (ns)<br>±0.2 ns | A2 |
|-------|----------|-------------------|----|--------------------------------|----|
| 1     | 1        | 310               | 96 | 0.5                            | 4  |
|       | 2        | 600               | 87 | 3.0                            | 13 |
| 2     | 1        | 320               | 96 | 0.5                            | 4  |
|       | 2        | 620               | 90 | 3.0                            | 10 |
| 2     | 1        | 310               | 98 | 0.5                            | 2  |
| 3     | 2        | 620               | 87 | 3.0                            | 13 |
| 4     | 1        | 280               | 98 | 0.5                            | 2  |
|       | 2        | 610               | 82 | 2.9                            | 18 |
| 5     | 1        | 300               | 98 | 0.5                            | 2  |
| 5     | 2        | 630               | 83 | 3.0                            | 17 |
| 6     | 1        | 300               | 97 | 0.5                            | 3  |
|       | 2        | 650               | 82 | 3.0                            | 18 |
| 7     | 1        | 310               | 94 | 0.5                            | 6  |
|       | 2        | 650               | 89 | 3.0                            | 89 |
| 0     | 1        | 300               | 94 | 0.5                            | 6  |
| 8     | 2        | 650               | 88 | 3.0                            | 12 |
| 0     | 1        | 310               | 96 | 0.5                            | 4  |
| 9     | 2        | 650               | 89 | 3.0                            | 11 |
| 10    | 1        | 290               | 97 | 0.5                            | 3  |
| 10    | 2        | 660               | 83 | 3.0                            | 17 |
| 11    | 1        | 300               | 96 | 0.5                            | 4  |
| 11    | 2        | 660               | 84 | 3.0                            | 16 |

Table S4. (Continued)

| Point | Detector | τ1 (ps)<br>±50 ps | A <sub>1</sub> | τ <sub>2</sub> (ns)<br>±0.2 ns | A2 |
|-------|----------|-------------------|----------------|--------------------------------|----|
| 1     | 1        | 400               | 97             | 0.7                            | 3  |
| 1     | 2        | 700               | 86             | 3.7                            | 14 |
| 2     | 1        | 400               | 96             | 0.7                            | 4  |
| Z     | 2        | 700               | 94             | 3.7                            | 16 |
| 2     | 1        | 350               | 96             | 0.6                            | 4  |
| 3     | 2        | 700               | 87             | 3.7                            | 13 |
| 4     | 1        | 320               | 98             | 0.6                            | 2  |
|       | 2        | 700               | 84             | 3.7                            | 16 |
| 5     | 1        | 320               | 98             | 0.6                            | 2  |
|       | 2        | 700               | 85             | 3.7                            | 15 |
| C     | 1        | 300               | 98             | 0.6                            | 2  |
| 0     | 2        | 650               | 82             | 3.7                            | 18 |
| 7     | 1        | 300               | 97             | 0.6                            | 3  |
| /     | 2        | 600               | 86             | 3.3                            | 14 |
| 0     | 1        | 300               | 97             | 0.6                            | 3  |
| 0     | 2        | 600               | 88             | 3.2                            | 12 |
| 0     | 1        | 340               | 97             | 0.6                            | 3  |
| У<br> | 2        | 700               | 87             | 3.7                            | 13 |
| 10    | 1        | 300               | 96             | 0.6                            | 4  |
| 10    | 2        | 600               | 86             | 3.3                            | 14 |

**Table S4.** Values of time constants ( $\tau$ i) and normalized (to 100) pre-exponential factors (ai) obtained from the fit of the emission decays of the different points of the image shown in Figure A) 8, B) 9, C) S13 and D) S14.

#### 6. Acid responsive color changes of CPHATN-1a.



**Figure S15.** (a) UV-vis absorption spectra of **CPHATN** in DMSO solution at different concentrations  $(5.7 \times 10^{-7} \text{ M to } 9.5 \times 10^{-6} \text{ M})$ . Absorption intensity and wavelength at absorption maxima change upon varying concentration. The observed behavior without Beer-Lambert law indicates that **CPHATN** molecules form an assembly even at concentration of  $1 \times 10^{-6} \text{ M}$ . (b) UV-vis spectra of HCl-exposed solution of **CPHATN** dissolved in DMSO solution at different concentrations  $(5.7 \times 10^{-7} \text{ M to } 9.5 \times 10^{-6} \text{ M})$ . Upon filling vapor of HCl into a cell of the solution, spectral profiles of solutions with different concentrations became similar ones with the same wavelength of absorption maxima, indicating that addition of HCl enhances association of **CPHATN**.



**Figure S16.** (a) UV-vis spectra absorption of methyl ester derivative **4** in CHCl<sub>3</sub> solution at different concentrations  $(4.4 \times 10^{-7} \text{ M to } 1.8 \times 10^{-5} \text{ M})$ . The observed behavior meets Beer-Lambert law. (b) UV-vis absorption spectra of trifluoroacetic acid (TFA) solution of **4** dissolved in a CHCl<sub>3</sub> solution with varied molar ratio of TFA. Upon adding TFA into the solution, a very weak band appeared at ca.470 nm. No significant changes were observed upon adding TFA.



**Figure S17.** Color changes of **CPHATN-1(TCB)** upon exposing to HCl vapor. The color of as-formed crystals of **CPHATN-1(TCB)** changes even when the framework accommodating TCB molecules within the pores.



**Figure S18.** PXRD patterns of crystalline bulks of **CPHATN-1a** upon dropping 37%-HCl solution. (i) Before and (ii) after adding one drop of 37%-HCl, and (iii) after subsequent heating at 150 °C for 30 min on a hot plate.



**Figure S19.** Color changes of **CPHATN-1a** upon exposing to HCl vapor. (a) Just after and (b) after 15 min laid in HCl vapor under ambient condition.



**Figure S20.** PXRD patterns of crystalline bulks of **CPHATN-1a** upon exposing to HCl vapor. Exposure to HCl vapor resulted in appearance of new peaks (red arrows), which then disappeared after removal of HCl by heating.



**Figure S21.** (a) Magic-angle emission decays of the ensemble solid of **CPHATN-1a** after exposing during 40 minutes in 37%-HCl atmosphere, upon excitation at 470 nm, and recording at the indicated wavelengths. The solid lines are from the best global fit using a multiexponential function. (b) Comparison between the ensemble solid of **CPHATN-1a** before (Squares) and after (circles) exposing during 40 minutes in 37%-HCl atmosphere, upon excitation at 470 nm.

| Sample                         | λ <sub>obs</sub><br>(nm) | τ1 (ps)<br>±30 ps | A <sub>1</sub> | <b>C</b> 1 | τ2 (ps)<br>±50 ps | A2 | <b>C</b> 2 | τ3 (ns)<br>±0.2 ns | <b>A</b> 3 | C3 |
|--------------------------------|--------------------------|-------------------|----------------|------------|-------------------|----|------------|--------------------|------------|----|
| Encomble                       | 530                      |                   | 94             | 74         |                   | 6  | 16         |                    | -          | -  |
| solid of                       | 550                      |                   | 92             | 62         |                   | 6  | 20         |                    | 2          | 18 |
| CPHATN-1a                      | 575                      | 72                | 88             | 46         | 260               | 9  | 23         | 1 0 1              | 3          | 31 |
| after HCl                      | 600                      | 13                | 81             | 32         | 300               | 14 | 26         | 1.01               | 5          | 42 |
| atmosphere                     | 625                      |                   | 71             | 20         |                   | 21 | 28         |                    | 8          | 52 |
| $\lambda_{\rm exc}=4^{2}/0$ nm | 650                      |                   | 63             | 14         |                   | 26 | 28         |                    | 11         | 58 |

**Table S5.** Values of time constants ( $\tau$ i), normalized (to 100) pre-exponential factors (ai) and contributions (ci= $\tau$ i x ai) obtained from a global multiexponential fit of the emission decays of the ensemble solid of **CPHATN-1a** after exposing during 40 minutes in 37%-HCl atmosphere upon excitation at 470 nm and observation as indicated.

## 7. NMR spectra of the compounds synthesized in this study.



Figure S22. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of diaminobenzene derivative 2.



Figure S23. <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of diaminobenzene derivative 2.



Figure S24. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of methyl ester derivative 4.



Figure S25. <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of methyl ester derivative 4.



Figure S26. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>, 100 °C) of CPHATN.



Figure S27. <sup>13</sup>C NMR spectrum (100 MHz, DMSO-*d*<sub>6</sub>, 100 °C) of CPHATN.

#### 8. References

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